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OXIDATION OF A LOW-TEMPERATURE LIGNITE TAR PITCH

John S. Berber and Richard L. Rice

U.S. Department of the Interior, Bureau of Mines
Morgantown Coal Research Center, Morgantown, W. Va.

INTRODUCTION

As part of a broad program of coal research, Bureau of Mines scientists are conducting research on the characterization and upgrading of low-temperature tar. An important part of this work is the study of pitch from low-temperature lignite tar.

In the processing of tar obtained by low-temperature carbonization of coal, a residue or pitch is obtained that distills above 350° C and has physical characteristics intermediate between those of coke oven (high-temperature) tar pitch and those of petroleum bitumens. Low-temperature pitches are complex resinous masses of polymerized and polycondensed compounds. They are amorphous, solid or semisolid plastic materials, and consist predominantly of carbon with several percent by weight of hydrogen, somewhat less oxygen, nitrogen, and sulfur, and small amounts of inorganic materials. They are chemically similar to the tars from which they are prepared, being mainly mixtures of the higher homologs of the compounds contained in the distillable fractions of the tar. The pitch fraction from low-temperature tar usually is 30 percent by weight or more of the tar, depending upon the source of the tar and processing conditions. There has been little demand for the material because it is hard and brittle. The Bureau of Mines is attempting to modify this pitch to convert it into a more marketable product.

One method that has worked with high-temperature pitches is to blow air through the pitch mass while the mass is being heated. Other methods include solvent refining, the use of additives, the use of catalysts, and thermal treatment in an inert atmosphere. This paper discusses the results of air-blowing tests designed to convert pitch into a material useful as electrode binder.

ELECTRODE BINDER PITCH

Pitch is used as a binder in the manufacture of four major classifications of electrodes: baked-in-place (cathodes), Soderberg, preformed baked, and graphitized high density. To make each of these types, the aggregate is mixed with the solid or melted pitch in a special mixer until the aggregate is completely coated. The mixture is then rammed in place, extruded or molded into the desired shape, then baked (2).*

* Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Soderberg electrodes are produced by mixing pitch binder with a graded aggregate of calcined petroleum coke, pitch coke, anthracite coal, bituminous coal coke, or mixtures of these. In the aluminum industry, only calcined petroleum or pitch coke is used to make electrodes to keep the impurities at a minimum.

So little is known about the structure or exact chemical composition of pitches that it is not possible to establish specifications other than by reference to arbitrary tests. Generally, the main properties involved in specifications for electrode binder, besides the softening point and carbon-to-hydrogen ratio, include specific gravity, coking value, ash content, distillation test, the amounts insoluble in benzene and soluble in quinoline, and the concentration of iron, silica, sulfur, and boron.

Softening point is particularly important in the production of electrode binder because the binder must be soft enough to properly mix with the electrode carbon and still contain enough resins to impart the desired compressive strength to the finished electrode. For electrode binder, the softening point should be about 95° to 110° C for Soderberg electrodes and 105° to 115° C for prebaked electrodes.

Electrode binder pitch must contain at least 20 percent of so-called "beta-resin," which is that portion soluble in quinoline, but insoluble in benzene (3). Concentrations of tar acids, tar bases, paraffins, saturated cyclic compounds, olefins, and alkyl groups attached to aromatic nuclei must be minimal because an excess of these adversely affect the properties of the pitch (1).

Carbon-hydrogen ratio is another property that pitch users consider of importance as it is an indication of plasticity, ductility, and elasticity of the binder. Most high-temperature pitches have a carbon-hydrogen ratio of about 1.8. The low-temperature pitch from lignite used in the tests in this report, however, had a carbon-hydrogen ratio of only about 0.84, and a low-temperature pitch from a bituminous coal had a C-H ratio of about 1.0. It can be readily seen that the C-H ratio of the low-temperature tar pitch must be increased if the material is to more nearly resemble commercial pitches.

The pitch used in these tests was obtained by batch distillation, under vacuum, of a low-temperature tar produced by the Texas Power and Light Company from Sandow lignite. Properties of the pitch are given in Table 1.

AIR-BLOWING OF PITCH

Since the binder characteristics of low-temperature tar pitch differ from those of high-temperature tar pitches, the pitch must be modified or upgraded if it is to be used for that purpose. As indicated, blowing with air (or oxygen) has been used to convert certain high-temperature bituminous pitches into material meeting specifications. It is a means of increasing the binder resin content of the pitch. The oxygen in the air acts as a condensation and dehydrogenating agent. The formation of water indicates that dehydrogenation has taken place, and the presence of carbon monoxide and carbon dioxide in the exit gases shows carbon has been lost. Little combined oxygen is found in the oxidized pitch.

As mentioned previously, a high carbon-to-hydrogen ratio appears a requisite for an acceptable electrode binder. Softening point and carbon-to-hydrogen ratio were taken as criteria of the effectiveness of the air-blowing treatment of these experiments to produce an electrode binder.

RESULTS

In the tests, the pitch was placed in a reactor (Figure 1), heated to the desired temperature, air or oxygen admitted at 2 to 4 scfh per pound, and agitation started at about 925 rpm. Runs ranged from 1 to 5 hours in length. Results are tabulated in Table 2.

It was found that the softening point generally increased in proportion to the length of time the air was blown through the pitch. The data plotted in Figure 2 illustrate the trend for air rates of 2.7 to 3 scfh per pound. Figure 2 also shows that for fixed run lengths, the softening point went up with increase in temperature of the heated mass.

Figure 3, a plot of reaction temperature versus softening point, better illustrates the effect of temperature. Blowing with oxygen raised the softening point temperature more than blowing with air.

Air rate also affected the softening point (Figure 4). It is apparent that air-blowing gave a very wide range of softening points, depending upon the reaction conditions. These conditions must be controlled very closely to give reproducible results.

A limited number of tests were made to determine the effect of sulfur addition on the softening point. Table 3 gives these results. In general, no definite pattern is apparent to indicate a material advantage for this treatment.

Blending was investigated to a limited extent. Industrial pitches are produced by distillation from high-temperature coke oven tars selected and blended to give the properties desired in the finished product, which vary in the different uses (4). It appeared that blending of different pitches, as shown in Table 4, would give a product having predictable characteristics. These blends, evaluated by the United States Steel Corporation electrode binder testing laboratory, indicate that the blends do not compare favorably with the pitch from coke oven tar in such properties as apparent density, crushing strength, electrical resistivity, and CO_2 reactivity. Table 5 gives the properties of the test electrodes.

CONCLUSIONS

This study on the air-blowing of pitch from low-temperature lignite tar was undertaken to prepare an effective electrode binder possessing properties of a bituminous pitch. Except for softening temperature, none of these properties were attained. The carbon-hydrogen ratio was increased slightly, but not significantly, and was below that of the blends made with high-temperature bituminous coal pitch which did not produce acceptable electrodes. Addition of sulfur does not significantly increase the carbon-hydrogen ratio. Either the blowing procedure was inadequate or air oxidation is not an effective means of upgrading low-temperature lignite tar pitch.

REFERENCES

1. Greenhow, E. J., and J. W. Smith. The Structure of Coal Tar Pitch. Australian J. Appl. Sci., v. II, No. 1, 1960, pp. 169-179.
2. Jones, H. L., Jr., A. W. Simon, and M. H. Wilt. A Laboratory Evaluation of Pitch Binders Using Compressive Strength of Test Electrodes. J. Chem. and Eng. Data, v. 5, No. 1, January 1960, pp. 84-87.
3. Lang, E. W., and J. C. Lacey, Jr. Low-Temperature Carbonization of America Seam Coal. Ind. and Eng. Chem., v. 52, No. 2, February 1960, pp. 137-140.
4. Thomas, B. E. A. Electrode Pitch. Gas World, v. 151, No. 3946, April 2, 1960, (Coking Supp., v. 56, No. 564), pp. 51-66.

TABLE 1. - Typical composition and properties of pitch before air-blowing compared with the desired properties

Properties	Typical	Desired
Softening point, °C	90[1]	95-110
Analysis, weight-percent		
Moisture	0.00	0.00
Carbon	83.78	92-93
Hydrogen	8.27	4-4.5
Sulfur	1.04	< 1.00
Nitrogen	1.06	1.00
Oxygen[2]	5.71	1-2
Ash	0.14	< 0.3
C-H ratio, atomic	0.84	1.8
Solubility, weight-percent		
Benzene	87.1	60
Petroleum ether	31.9	10

[1] Ring-and-ball softening point.
[2] Oxygen obtained by difference.

TABLE 2. - Air-blowing of pitch from low-temperature lignite tar

Run no.	Length of run, hours	Temp., ° F	Air rate, scfh/lb	Softening point at start, °C	Softening point at end, °C	Carbon, wt-pct	Hydrogen, wt-pct	C-H atomic ratio
110	3	300	2	92	111	83.50	7.59	0.92
14	2	428	2	--	121	84.08	7.67	0.91
15	2.5	428	2	--	123	83.10	7.68	0.90
16	3	428	2	--	132	83.54	7.71	0.90
27	3.5	482	2	--	207	84.15	7.30	0.96
115	1	300	2.7	90	93	85.42	7.47	0.95
116	2	300	2.7	90	96	85.23	7.61	0.93
114	1	350	2.7	90	94	85.30	7.58	0.94
112	2	350	2.7	90	109	84.92	7.64	0.93
113	2	350	2.7	90	109	84.48	7.65	0.92
117	3	350	2.7	90	118	85.16	7.73	0.92
118	3.5	350	2.7	90	119	85.08	7.77	0.91
18	4	428	2.7	--	150	83.85	7.59	0.92
19	2	455	2.7	--	146	83.94	7.44	0.94
23	4	455	2.7	--	168	83.41	7.33	0.95
24	2	482	2.7	--	154	84.55	7.55	0.93
107	2.5	300	3	92	101	84.00	7.68	0.91
109	3	300	3	92	111	83.90	7.45	0.94
78	5	334	3	--	159	83.80	7.47	0.93
7	1	400	3	--	108	83.72	7.97	0.88
6	1	455	3	--	129	83.00	7.90	0.88
26	3	482	3	--	185	84.04	7.22	0.97
2	1	500	3	--	166	83.59	7.68	0.91
1	2	500	3	--	202	84.58	7.54	0.93
95	1	300	4	76	95	84.00	7.43	0.94
46	2	482	4	--	175	84.00	7.29	0.96

TABLE 3. - Pitch blown with oxygen, nitrogen, and air, with sulfur added

Run no.	Length of run, hours	Temp., °F	Rate, scfh/lb	Carbon, wt-pct	Hydrogen, wt-pct	C-H atomic ratio	Softening point, °C	Softening point before treating, °C	Sulfur, pct
Oxygen									
41	2	428	0.3	83.25	7.61	0.91	123		
42	3.5	527	0.4	86.79	6.74	1.07	> 250		
44	4	500	0.3	83.20	7.20	0.96	> 250		
49	3	482	0.27	85.49	7.13	0.99	> 250		
121	1	275	0.57	84.98	7.68	0.92	108	105	
122	1	275	0.57	85.19	7.74	0.92	117	105	
123	2	300	0.57	85.35	7.68	0.93	121	105	
124	1	275	0.57	84.69	7.78	0.91	113	105	
54	5	400	0.27	84.17	7.33	0.96	> 250		5
57	2	400	0.27	83.28	7.76	0.89	130		3
58	2	428	0.27	83.30	7.78	0.89	141		3
59	2	455	0.27	84.10	7.48	0.94	172		3
Nitrogen									
60	2	400	2.7	83.47	7.85	0.89	136		3
61	4	400	2.7	83.44	7.75	0.90	123		3
62	4	455	2.7	83.50	7.65	0.91	121		3
63	4	500	2.7	83.72	7.68	0.91	129		3
66	2	482	2.7	83.78	7.76	0.90	118		3
67	2	482	2.7	83.76	7.80	0.89	121		3
68	4	482	2.7	83.58	7.70	0.90	121		3
69	23.65	482	2.5	84.09	7.17	0.98	178		3
71	31.25	482	2.7	84.15	7.18	0.98	> 250		5
Air									
55	5	400	2.7	83.39	7.21	0.96	> 250		5
56	3	400	2.7	83.40	7.44	0.93	177		3
132	1	282	2.7	81.60	7.57	0.90	105	90	5
135	1	240	3	84.76	7.55	0.94	111	93	5
136	1	350	3	84.79	7.52	0.94	112	93	5
137	1	420	3	84.86	7.56	0.94	124	93	5
138	1	470	3	85.30	7.44	0.96	132	93	5
139	1	440	3	85.18	7.47	0.95	128	93	5
140	1	410	3	85.00	7.52	0.94	116	93	2.5

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TABLE 4. - Data on samples evaluated by U.S. Steel for electrode binders

Properties	Pitch blends No. 1[1]	Pitch blends No. 2[2]
Carbon	86.05	85.73
Hydrogen	6.40	6.39
C-H ratio	1.12	1.12
Softening point, °C	106	105
Penetration	0	0
Benzene insolubles	30	24

[1] 60 Percent low-temperature tar with softening point of 110° to 112°C and 40 percent high-temperature tar with softening point of 104° to 108° C.

[2] 60 Percent low-temperature tar with softening point of 97° to 101°C and 40 percent high-temperature tar with softening point of 110° to 121°C.

TABLE 5. - Properties of electrodes prepared with Bureau of Mines binders

Properties	Bureau of Mines pitch blends No. 1	Bureau of Mines pitch blends No. 2	U.S. Steel coke oven pitch
Optimum binder content, wt-pct[1]	34	31	34
Apparent density, g/cm^3	1.32	1.38	1.46
Electrical resistivity, ohm-cm x 10^{-4}	79.3	72.0	59.2
Crushing strength, kg/cm^2	302	388	642
CO_2 reactivity, mg/g/hr	79.5	74.5	74.3
Dust, wt-pct	10.4	6.4	3.1

[1] Standard commercial aggregate, mix temperature 155° C.